Phonons from Density Functional Theory for Equations of State

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Phonons cannot be neglected in the construction of a material's equation of state (EOS); they tend to be the main thermal contribution to the free energy. The construction of reliable EOS for the Sesame database from density functional theory (DFT) thus requires the phonons be calculated from DFT. It also requires knowing the reliability of the calculated phonons' accuracy with respect to experiment. We have extensive experience that guides us in knowing the reliability of calculated cold curves; more recent experience sheds light on the reliability of DFT phonon calculations.

For example, the phonon dispersion for hexagonal close-packed (hcp) beryllium shown in Fig. 1 gives an idea of how exact the DFT results can be expected to be. The calculated frequencies agree very well with experiment along the acoustical branches. The differences in the optical phonon frequencies is roughly 10% between results from the two DFT methods used—APW+lo (augmented plane wave plus local orbitals) and PAW (projector-augmented wave). Differences of roughly 10% also appear between either method's results and the experimental data. In our experience this is typical: for most materials DFT calculations and experiment agree very closely on the acoustic mode frequencies and within 10% on the optical mode frequencies.

The details of the phonon dispersion are less important in the construction of a reliable EOS than is the overall phonon density of states (DOS). The phonon DOS determines the contribution to the free energy via weighted frequency integrations of the DOS, i.e., the details of the dispersion are washed out in the process. In practice we calculate the volume-dependent phonon DOS at a sequence of volumes (shown, e.g., in Fig. 2 for tantalum), and from these we evaluate the Helmholtz free energy F(V,T). Interpolating F(V,T) as a function of volume results in the EOS.

The Helmholtz free energy F(V,T) can be transformed into the Gibbs free energy G(P,T). Comparison of the Gibbs free energies G(P,T) of two phases leads to predictions for structural phase transitions, e.g., the hcp to bcc transition for beryllium shown in Fig. 3. At low pressure our calculations predict a phase transition around 400 GPa, in agreement with experiment, where no transformation has been observed up

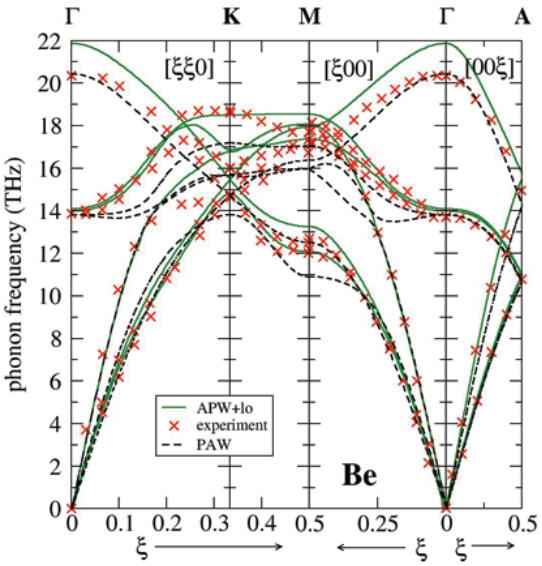

Fig. 1.
Phonon dispersion for beryllium in the hexagonal close-packed structure at the experimental equilibrium geometry. The calculated phonon frequencies agree well with the experimental values, especially for the acoustic branches. The agreement between experiment and theory for the optical branches is within 10%, similar to the agreement between the values calculated with the two DFT methods.

to the maximum pressure achieved to date, 180 GPa. For the low pressure, high temperature transition our results disagree strongly with experiment: the measured ambient pressure transition occurs at a temperature of 1530 K whereas theory predicts the transition to take place near 6000 K. This discrepancy reflects the neglect of strong anharmonicity in our current calculations.

Strong anharmonicity appears in many other elements where the bcc phase appears at high temperatures as well as in the low-temperature hcp phase of Zr and alpha phase of U. The inclusion of strong anharmonicity effects is thus a challenge we are working to overcome as we strive to make DFT more reliable in the construction of equations of state.

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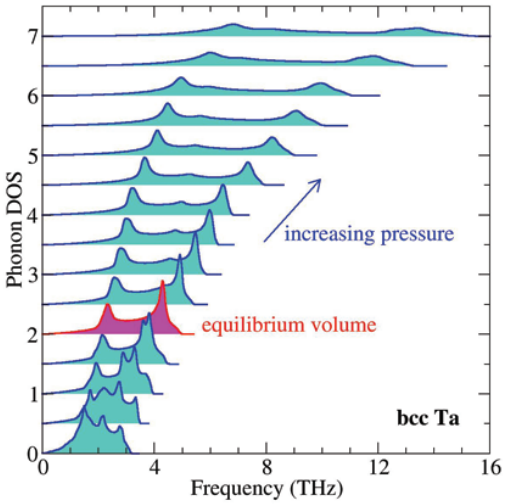

Fig. 2.
Calculated phonon density of states for tantalum in the body-centered cubic structure at a sequence of volumes.

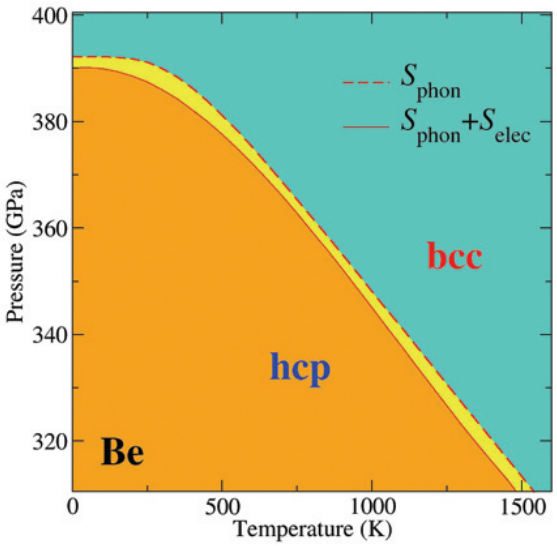

Fig. 3.
Calculated hcp-to-bcc phase transition line for beryllium. The phonons make up the largest contribution to the temperature dependence of the phase transition; the electronic contribution lowers the transition pressure only slightly.